# GEIGER

## The use of Coagulants in the Application of Enamels to Plastic Clay Bodies

Ceramic Engineering

B. S.

1915

# THE USE OF COAGULANTS IN THE APPLICATION
# OF ENAMELS TO PLASTIC CLAY BODIES

BY

## CHARLES FRANCIS GEIGER

## THESIS

FOR THE

## DEGREE OF BACHELOR OF SCIENCE

IN

## CERAMIC ENGINEERING

## COLLEGE OF LIBERAL ARTS AND SCIENCES
## UNIVERSITY OF ILLINOIS

1915

# UNIVERSITY OF ILLINOIS

June 1, 1915

THIS IS TO CERTIFY THAT THE THESIS PREPARED UNDER MY SUPERVISION BY

Charles Francis Geiger

ENTITLED THE USE OF COAGULANTS IN THE APPLICATION OF ENAMELS

TO PLASTIC CLAY BODIES

IS APPROVED BY ME AS FULFILLING THIS PART OF THE REQUIREMENTS FOR THE

DEGREE OF Bachelor of Science

in Ceramic Engineering

*R. T. Stull*

Instructor in Charge

APPROVED: *R. T. Stull*

HEAD OF DEPARTMENT OF Ceramics

# TABLE OF CONTENTS

# THE USE OF COAGULANTS IN THE APPLICATION

# OF ENAMELS TO PLASTIC CLAY BODIES

## I

## INTRODUCTION

The method employed at present in the manufacture of enamel brick consists in applying an opaque, white engobe to the body and covering this with a glaze or somewhat opaque enamel.  Stull[1] gives the following groups based on the method of application of the engobe:-

    I   Hand Dipping Process.

        a.  Single Fire:-

            (1)  Dipping Stiff-Mud Brick,

            (2)  Dipping Leather-Hard Brick,

            (3)  Dipping Bone-Dry Brick.

        b.  Two Fire:-

            (1)  Dipping Biscuited Brick.

    II  Mechanical Veneering Process.

        a.  Single Fire:-

            (1) Veneering Stiff-Mud Column and Wire-Cutting.

---

1.  Trans. Am. Cer. Soc., Volume 12,  p. 712.
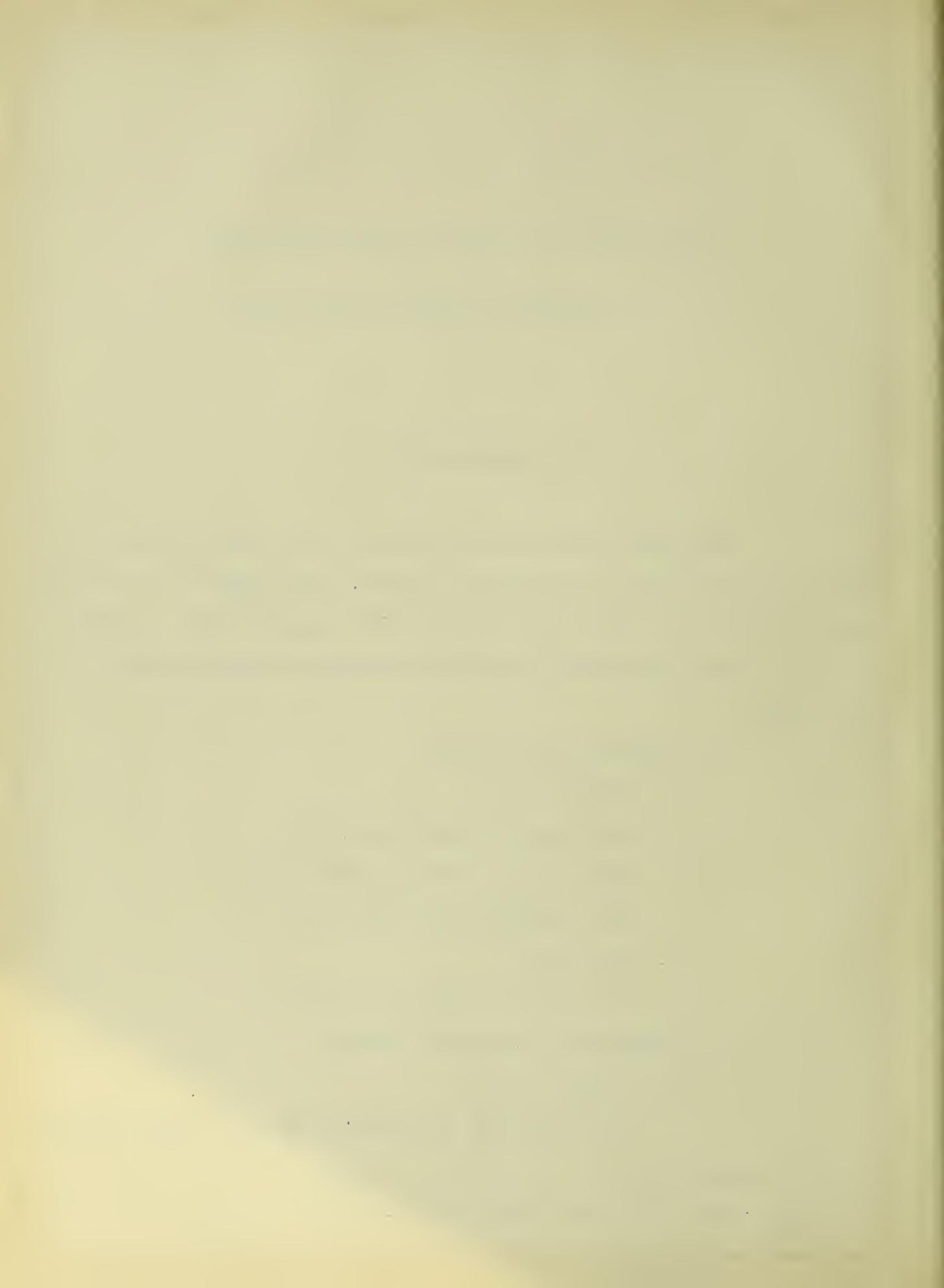
The preparation of the slip[2] is the same for all methods given under I. In the mechanical veneering process, however, after the slip has been ground or blunged it is first necessary to make it of such a fluid consistency that it can be readily screened; then to thicken it by filter-pressing and final pugging. The latter operations render the slip of uniform quality and of sufficient stiffness for use in the veneering machine. Inasmuch as the filter press is expensive to maintain and is a frequent source of trouble and cause of delay, it would be advantageous, if possible, to dispense with its use. The ideal method, in this instance, would be thinning of the slip with sufficient water for screening, subsequent thickening merely by the addition of suitable coagulating reagents, and pugging, thus eliminating the use of the filter press. Undoubtedly there is ample opportunity for improvement in any of the methods now used; and it was for the purpose of determining, if possible, if enamel brick could not be manufactured more economically than they are at present by reducing the cost of preparing the slip that this investigation was undertaken.

An attempt was made in the following work to regulate an enamel, (or opaque glaze) so that it might be applied directly by the veneering machine to the stiff-mud column from which the brick are to be cut.

By this method a noteworthy saving could be effected in the handling of the slip and of the brick and in the cost of coating.

---

2. The terms "slip" and "engobe" are used synonymously herein and mean the under-glaze coating. "Slips" will mean the thin mixtures of enamel and water mentioned on page 12.

The enamel would cost only little more than the glaze used at present; the increase in cost would be the expense of the additional $SnO_2$ necessary to use in the enamel; but this would still be considerably less than the cost of the under-slip and the glaze. The expenditures for handling, moreover, would be greatly decreased.

The extensive research of Kirkpatrick and Arnold[3] was along this line. They worked with several fireclay mixtures and a number of enamels, determining the effects of several electrolytes and other substances upon the fitting of their enamels. Their chief conclusion is: "that it is possible to regulate the shrinkage and adhesion of enamels when applied to stiff mud bodies by means of the inorganic colloid, silicic acid, precipitated in the enamels by means of oxalic acid " and sodium silicate: they found also, that the precipitation of colloidal silicates in the enamel did not produce bonding power; that the precipitation of colloidal silica by hydrochloric acid and sodium silicate would not effect the desired results; that salts, though increasing viscosity failed to produce bond; that acids alone gave no bonding power to the enamel; and that not enough clay to produce adhesion could be used in the enamel because of the dulling effect on the burned coating.

The "regulation" of the enamel consists in controlling the shrinkage and the adhesive power. These, it was hoped, could be governed by the addition of some electrolyte. As sodium carbonate has done so much for the casting process in the sanitary clay-ware industries, it was thought possible that some other electrolyte,

---

3. The Effect of Electrolytes, and Inorganic Colloids, on the
   Mechanical Fitting of Enamels to Plastic Clay Bodies.
   Thesis, University of Illinois, 1914, p. 73.

a coagulator in this case, could be found that would increase the

bonding power of an enamel and allow adjustment of its shrinkage.

Kirkpatrick and Arnold[4] say: "The best conditions for
perfect mechanical fit between a slip and a plastic body are that
the amount of shrinkage and the rate of shrinkage of the slip should
be the same as that of the plastic body and adhesion between the
slip and body must result."

It was found that the difficulties to be overcome are

principally flaking and cracking.

"Flaking or shelling of the slip," says Stull[5] "is due
to lack of bond.  It may occur soon after dipping or may not appear
until the brick are subjected to the fire.  Lack of bond may be
caused by oil or dust on the surface or by  unequal shrinkage of
slip and body.  It is most frequently caused by too low shrinkage
of the slip, but in some cases it is caused by too high shrinkage
of the slip.  In the latter case flaking and cracking will occur
on the same surface......... Where flaking is due to low shrinkage,
the remedy is to increase the percent of plastic clay and decrease
the non-plastic portion.  Where cracking and flaking occur, re-
duce the percent of clay and substitute part ball clay for china
clay or kaolin.

"The tendencies of ball clay are to increase shrinkage,
impart greater adhesive power, and render the slip more yielding
or ductile by which it adjusts itself better to the brick, thus
preventing rupture."

Also: "Cracking may be caused by: 1. Excessive shrinkage
of the slip.  2. Too thick coating of the slip.  3. Too fine grind-
ing of slip.  4. In dipping leather hard, allowing the brick to
become too dry before dipping.  5. Using clays which are weak or
have low tensile strength.

"Cracking may be overcome by substituting a clay of low
shrinkage for one of higher; or increasing the non-plastic portion
and decreasing the plastic part, such as increasing flint and feld-
spar or Cornwall stone or replacing part raw clay with calcined
clay."

---

4.   The Effect of Electrolytes, and Inorganic Colloids, on the

Mechanical  Fitting of Enamels to Plastic Clay Bodies. p.2.

5.   Trans. Am. Cer. Soc., Volume 12, p. 717.

These remedies though given for a slip ought to be applic-
able for an enamel. However, the requirements of the burned enamel
limit the amount of clay to about 30 per cent so that recourse must
be had in other methods. The alternative is to increase the quanti-
ty of colloidal gel in the enamel without addition of clay. This
may be accomplished by addition of some electrolytes or by the direct
addition of a gel. Both were tried in this work.

II

METHODS.

Kirkpatrick and Arnold attempted to increase the amount
of colloidal gel by the addition of electrolytes but obtained no
encouraging results with the exception, possibly, of silicic acid
precipitated from sodium silicate by oxallic acid. In this work
the writer tried a few electrolytes used by Kirkpatrick and Arnold
and several others together with two different organic colloids
not employed by them. The effect of Stanic Chloride, magnesium
sulphate, alum, sodium silicate and oxallic acid, washed silicic
acid, starch, and gum tragacanth was tested.

Some method was necessary for observing the effects of
the reagents upon the enamel. Since the viscosity of colloidal
solutions is highly sensitive to the action of electrolytes the
measurement of that factor was decided upon.

The instrument used was a
Mariotte tube of about 1-1/3 inches
diameter. The efflux tube was of
two millimeters and the air tube of
four millimeters inside diameter.
The viscosity of water was consider-
ed unity and the time of flow for
this standard fluidity was deter-
mined on each day that any viscos-
ity determinations of the enamels
were made.



Mariotte Tube.

-6-
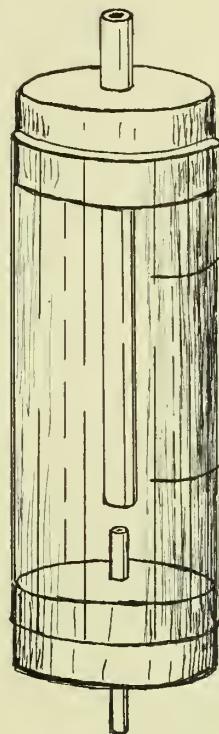
Often those manufacturers of sanitary and other ware that use the casting process complain that after their slips have stood for long periods they give inferior products. It is for this reason that special attention was paid in this work to the time effect of the reagents and that viscosity tests were made every day for one or sometimes two weeks. The viscosities as given in the table are the averages sometimes of only two determinations but often of five or six;when the time ran well into minutes, however, usually only one test was made.

Assuming that if a regulator were found for an enamel it would serve the same purpose to a degree in almost any other simi- lar mixture, only one enamel was used. It is one used by Kirkpat- rick and Arnold. The formula is:-

$$
\left.\begin{array}{l}
.10 \ K_2O \ ) \\
\qquad\qquad ) \\
.20 \ CaO \ ) \\
\qquad\qquad ) \ .64 \ Al_2O_3 \\
.35 \ CaO \ ) \\
\qquad\qquad ) \\
.35 \ ZnO \ )
\end{array}\right\}
\begin{array}{l}
) \ 3.8 \ SiO_2. \\
) \\
) \ 0.12 \ SiO_2.
\end{array}
$$
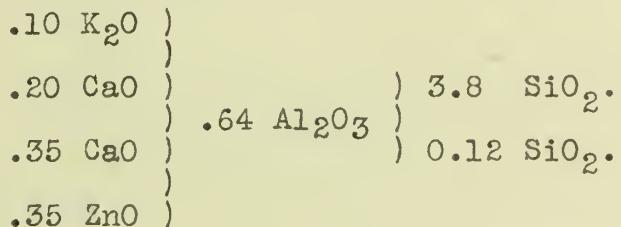
The batch proportions are:-

| | |
|---|---|
| Brandywine Spar | 127 |
| Whiting | 80 |
| Barium Carbonate | 89 |
| Zinc Oxide | 65 |
| Flint | 290 |
| Pikes #20 English Ball Clay | 100 |
| M. G. R. English China Clay | 150 |
| Calcined M. G. R. English China Clay | 58 |
| Tin Oxide | 41 |
| | 1000 |

From this it is seen that the raw clay is twenty-five per cent of the batch.

The materials for the glaze were screened and ground in porcelain ball mills with almost 100 per cent of water for one and one-half to two hours. The enamel was then passed thru a 100 mesh screen and allowed to age for about two weeks. Then the moisture factor of a small sample was determined and the remainder sealed in jars.

The consistency of the first batch of enamel was such that 100 grams of the liquid suspension contained forty-nine grams of solid matter; while 100 grams of the second batch contained fifty-two grams of dry material. The first supply was sufficient for series one to four inclusive, and the second served throughout the remainder of the work.

For the viscosity tests enough of the liquid enamel was weighed into each of a number of graduated cylinders to give either forty or fifty grams of solid materials (the amount used for each series is given later.) Then the electrolyte was introduced and water added to bring the total volume to 100 c.c. in each case. The cylinders were shaken thoroughly, allowed to stand, and shaken again. In the daily tests shaking was necessary for long periods previous to the viscosity measurements as usually there was considerable settling over night.

For the adhesion and cracking tests small trial pieces of fireclay and grog mixtures were used. These were about one and one-half inches square and five-eighths inch thick. The following compositions were used and marked as indicated:-

```
      ) 67 %  Templeton Clay.
  O   )
      ) 33 %  Grog.


      ) 70 %  Bloomingdale Stoneware Clay.
  I   )
      ) 30 %  Grog.


      ) 70 %  St. Louis Fire-clay.
  II  )
      ) 30 %  Grog.
```

The trials were made stiff-mud and kept in this condition in a moist can. Those used for the first six series, however, were slightly dryer than stiff-mud yet not leather hard. Then it was discovered that the pieces could be preserved as soft as when made by being kept in contact with damp burlap in the moist can. The trial pieces of bodies O and I used in the last seven series were even softer than when molded.

Dipping the trials consisted in pouring the enamel on the surface and agitating the pieces slightly so that the coatings would spread evenly. First, however, the trials were scrubbed with a soft brush and water in order to roughen up the surface so that better opportunity for adhesion was provided. The enamels used in the viscosity tests were used in the dipping just after the last set of viscosities had been determined. The dipped trials were set in a cardboard box with a loose cover and allowed to dry very slowly. After four or five days the cover was removed, and in another day or so the trials were taken from the box and air-dried.

The following symbols will be used in indicating the results:-
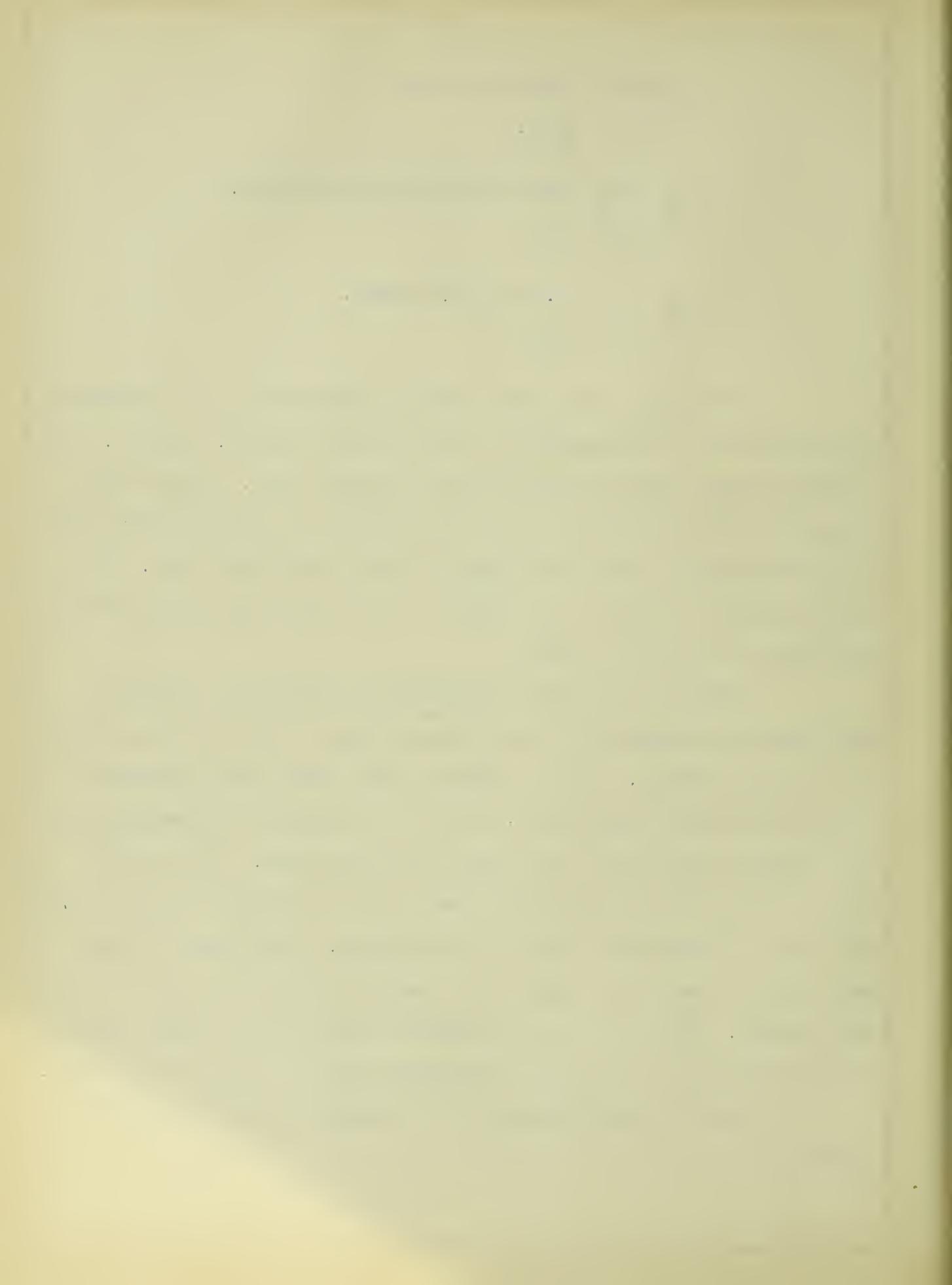
C - Cracked.

F - Flaked.

G - Good, having all desirable properties.

NB- No bond.

SB- Slight bond.

FB- Fair bond.

GB- Good bond.

# III

## DATA AND RESULTS

### Series 1.

The first series was one containing additions of stannic chloride in varying amounts up to two per cent. A solution of $SnCl_4 \cdot$ ? $H_2O$ containing forty grams per liter was made. The use of this reagent was attempted since it is known that salts in which the metals have the highest valence are the most effective coagulators. In the case of stannic chloride the valence of the tin is four.

Hatschek[6] gives a table showing that the coagulating powers of molecular equivalents of ordinary salts of the same base; namely, Potassium, Barium, and Aluminum are remarkably nearly equal; that is the same molecular concentrations of aluminum chloride and aluminum nitrate, for example, are equally effective in the coagulation of any one sol. This indicates that the basic ion alone is responsible for the action. On this account there is little likelihood of our acquiring sufficiently coagulated slips through the use of an electrolyte, if another containing the same cation has failed to give results. Another important conclusion that may be deduced from the table concerns the relation between the thickening effect and the valence of the cation causing the coagulation. The specific data are that univalent cations exert only about one seventy-fifth and one six hundreth the coagulating effects of divalent and trivalent cations respectively. No figures are given for quadrivalent ions but they would undoubtedly be correspondingly higher.

6. An Introduction to the Physics and Chemistry of Colloids, p 33.

In series 1, enough of the fluid enamel was used to give fifty grams of solid material in each sample. In twenty-four hours however, the slips had become so thickened that they had to be abandoned because of the long time required for each flow test.

The results of the viscosity tests follow. The factor given is the time of flow for water; this was determined every day because of temperature differences and because the same divisions on the Mariotte tube were not used from day to day. The time of flow in seconds may be obtained in any instance by multiplying the given factor by the corresponding time.

VISCOSITIES = SERIES 1

$SnCl_4 \cdot$ ? $H_2O$ + 50 grams Solid Material.

| | | Hours | |
|---|---|---|---|
| | | 2 | 24 |
| Factor | | 13.4 | 13.4 |
| Number | % Reagent | | |
| 0 | 0 | 1.45 | 1.35 |
| 1 | .1 | 1.78 | 2.11 |
| 2 | .2 | 1.97 | 3.52 |
| 3 | .3 | 2.14 | 3.98 |
| 4 | .4 | 2.75 | 28.3 |
| 5 | .5 | 4.08 | 26.1 |
| 6 | .6 | 11.17 | 60.9 |
| 7 | .7 | 22.6 | 56.5 |
| 8 | .8 | 67.1 | 43.5 |
| 9 | .9 | 43.4 | 43.5 |
| 10 | 1.0 | 67.1 | 130.5 |
| 11 | 2.0 | 86.1 | 108.7 |

Because of the sudden drop in viscosity of number nine at two hours it was thought that perhaps a mistake had been made in the introduction of the electrolyte. However, the results obtained after two hours with a new sample checked.

-13-

FIGURE 1
SERIES 1
$SnCl_4 \cdot ?H_2O$.
REAGENT-VISCOSITY
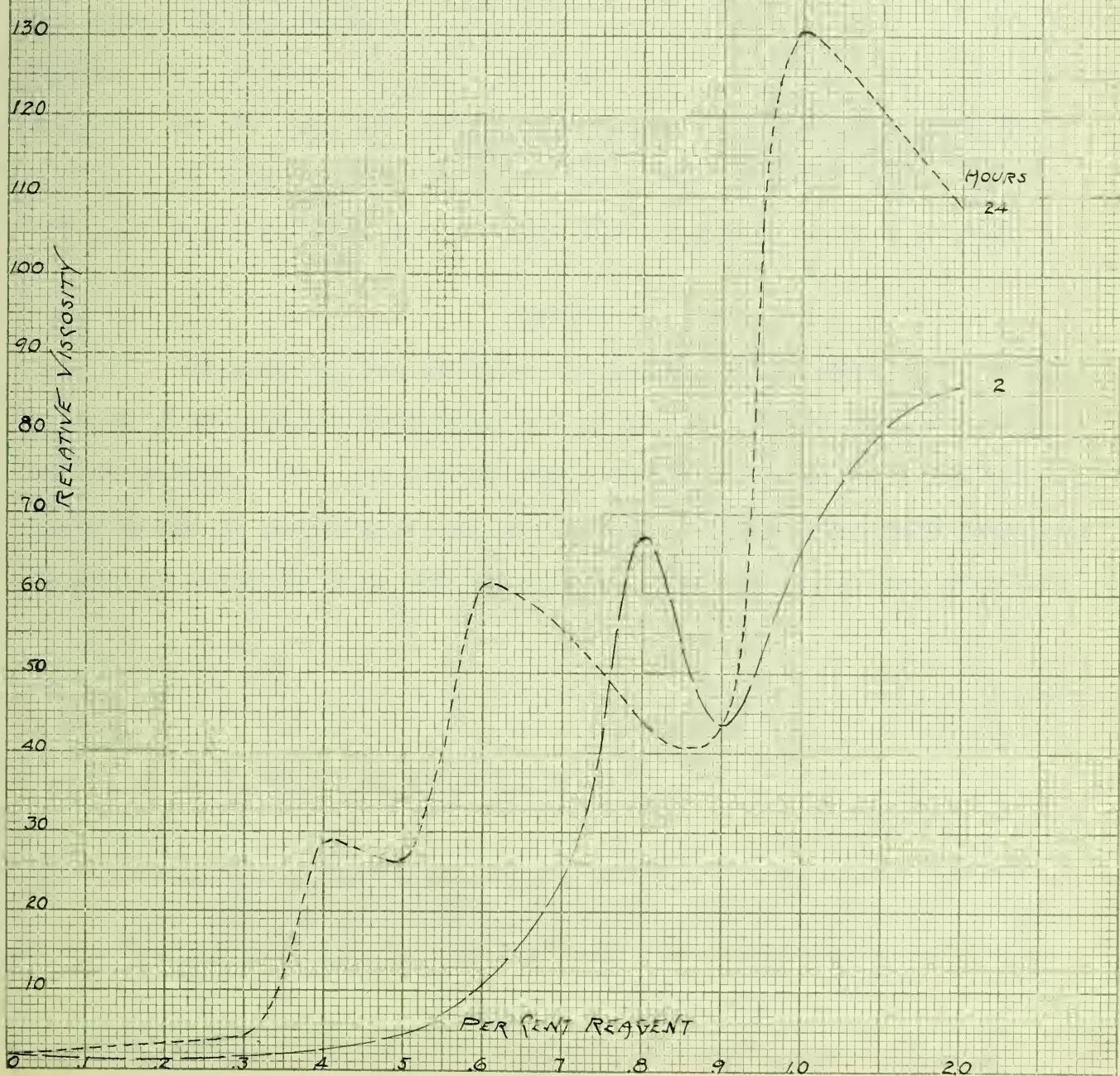
The 2 hour curve in Fig. 1 shows that increasing amounts of reagent up to .8% increased the viscosity. At .9% a minimum was reached after which viscosity again increased. The results at 24 hours are more irregular, three minimum points occur, one checking the first. In every case but one, however, the time effect was to increase the viscosity.

The test pieces were coated with the enamels just as they were after twenty-four hours. The properties of the dried trials are shown in the table:-

| Number | 0 | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 | 10 | 11 |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Body O | FB | F | FB | FB | FBSB | C,SB | C,SB | F | C,SB | C,SB | C,SB | C,SB |
| " I | FB | FB | FB | FB | NB | NB | FB | FB | SB SC | SB SC | SB SC | SB SC |
| " II | F,C | F,C | F,C | F,C | F,C | F,C | F,C | F,C | F,C | F,C | F,C | F,C |

## Series 2.

Because of the extreme viscosity of the samples of series 1, good flow measurements were not possible. Hence another set was necessary. The new series was exactly like series 1 except that forty grams of solid material were used. Viscosities were measured on six consecutive days and equilibrium had not then been attained.
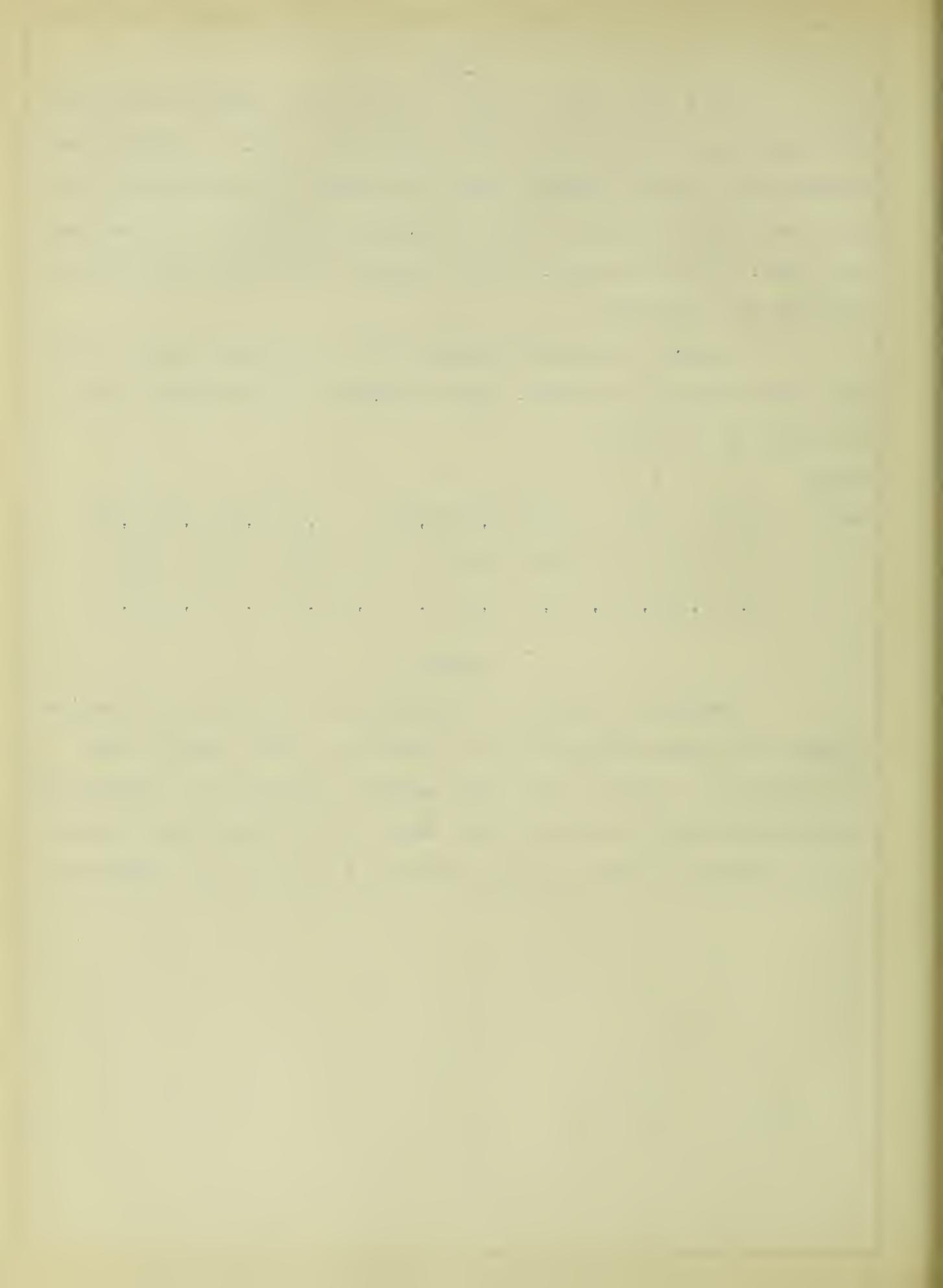
## VISCOSITIES - SERIES 2

$SnCl_4 \cdot ?$ $H_2O$ + 40 grams Solid Material.

| | | Hours | | | | | | |
|---|---|---|---|---|---|---|---|---|
| | | 1 | 3 | 24 | 45 | 75 | 98 | 120 |
| Factor | | 13.4 | 13.4 | 13.2 | 12.8 | 13.3 | 13.2 | 13.0 |
| No. | % Reagent | | | | | | | |
| 0 | 0 | 1.24 | 1.24 | 1.25 | 1.22 | 1.28 | 1.21 | 1.23 |
| 1 | .1 | 1.47 | 1.47 | 1.54 | 1.48 | 1.62 | 1.51 | 1.51 |
| 2 | .2 | 1.62 | 1.65 | 1.92 | 1.84 | 2.00 | 1.78 | 1.77 |
| 3 | .3 | 1.86 | 1.88 | 2.22 | 1.91 | 2.10 | 1.89 | 1.94 |
| 4 | .4 | 1.47 | 1.72 | 2.21 | 2.03 | 2.14 | 2.03 | 2.08 |
| 5 | .5 | 2.32 | 2.24 | 2.65 | 2.34 | 2.45 | 2.35 | 2.43 |
| 6 | .6 | 1.97 | 2.97 | 2.82 | 2.61 | 2.78 | 2.70 | 2.92 |
| 7 | .7 | 2.36 | 3.61 | 4.09 | 3.09 | 3.17 | 3.10 | 3.70 |
| 8 | .8 | 2.21 | 2.76 | 3.96 | 2.60 | 2.59 | 2.50 | 2.68 |
| 9 | .9 | 2.81 | 3.61 | 4.01 | 3.36 | 3.14 | 3.05 | 3.82 |
| 10 | 1.0 | 2.27 | 5.15 | 4.16 | 3.72 | 4.28 | 4.08 | 5.84 |
| 11 | 2.0 | 3.38 | 7.98 | 4.77 | 5.55 | 6.43 | 7.05 | 8.77 |

These data are plotted in the curves on pages 16 and 17. Fig. 2 shows that the maximum points check only with .7% reagent. In all cases, however, 2% shows a relatively high viscosity at increasing time intervals, and an increase in viscosity occurs rather regularly with all additions up to .7%. From Fig. 3 it is observed that except in the cases of samples numbered 6, 10, and 11, maximum viscosity is attained in 24 hours. With No. 11 a minimum results at that time.

The enamels of series 2 were applied only to body O with the following results:-

| Number ) | 0 | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 | 10 | 11 |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Body O ) | SB | F,C | F,C | F,C | F,C | F,C | F,C | F,C | F,C | F,C | F,C | F,C |

Thus it is noted that while stannic chloride coagulated the enamel it afforded no bonding power.

-16-

FIGURE 2
SERIES 2
$SnCl_4 \cdot 7H_2O.$
REAGENT-VISCOSITY

RELATIVE VISCOSITY

PER CENT REAGENT

HOURS.
120
3
98
75
45
24
1
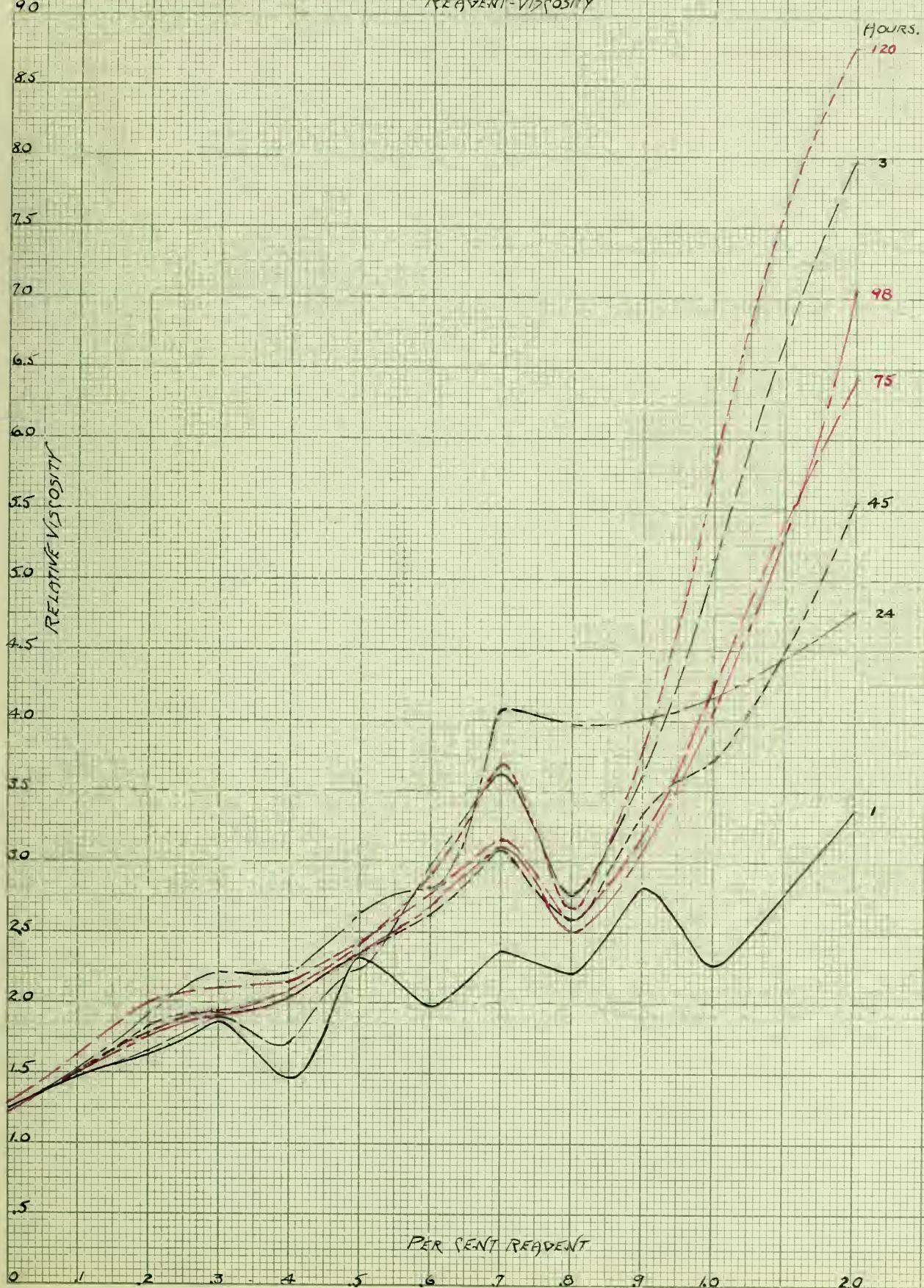
-17-
FIGURE 3
SERIES 2
$SnCl_4 7H_2O$
TIME - VISCOSITY
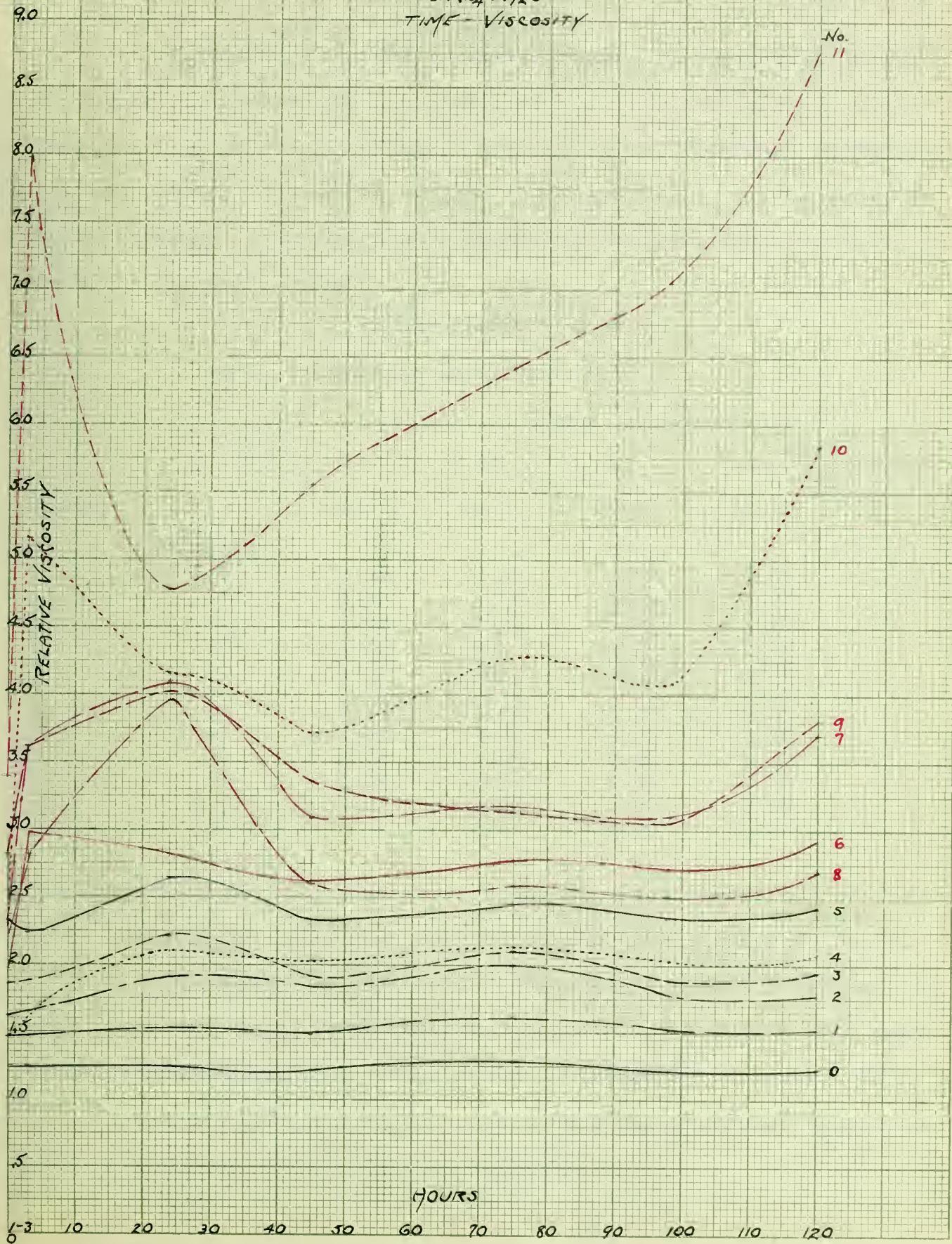
## Series 3.

Magnesium sulphate in small amounts is frequently added to enamels for sheet steel in order to hold the particles in suspension; i.e. prevent settling. Evidently the "floating" is accomplished through conversion of some colloidal sol to gel by the coagulant $MgSO_4$. This phenomenon suggested the employment of this reagent in a test series.

### VISCOSITIES - SERIES 3

$MgSO_4$ + 40 grams Solid Material.

| | | Hours | | | |
|---|---|---|---|---|---|
| | | 3 | 24 | 54 | 78 |
| Factor | | 13.2 | 12.8 | 13.3 | 13.2 |
| No. | % Reagent | | | | |
| 0 | 0 | 1.24 | 1.44 | 1.26 | 1.21 |
| 1 | .1 | 1.27 | 1.39 | 1.29 | 1.21 |
| 2 | .2 | 1.29 | 1.41 | 1.28 | 1.21 |
| 3 | .3 | 1.29 | 1.39 | 1.22 | 1.14 |
| 4 | .4 | 1.32 | 1.46 | 1.32 | 1.26 |
| 5 | .5 | 1.35 | 1.46 | 1.35 | 1.27 |
| 6 | .6 | 1.33 | 1.45 | 1.37 | 1.28 |
| 7 | .7 | 1.33 | 1.48 | 1.38 | 1.33 |
| 8 | .8 | 1.36 | 1.50 | 1.40 | 1.33 |
| 9 | .9 | 1.36 | 1.53 | 1.41 | 1.33 |
| 10 | 1.0 | 1.36 | 1.49 | 1.40 | 1.39 |
| 11 | 2.0 | 1.40 | 1.61 | 1.50 | 1.42 |

The slips were so thin that the viscosities were almost too uniform to be comparable. They were applied to the trials after 78 hours.

The curves of Fig. 4 show gradually increasing viscosities with increasing amounts of reagent, while those of Fig. 5 show most excellently that maximum viscosity was attained in 24 hours. Hence if this reagent should give the requisite bond the enamel should be used twenty four hours after its addition.

-19-

FIGURE 4

SERIES 3

MgSO₄

REAGENT-VISCOSITY
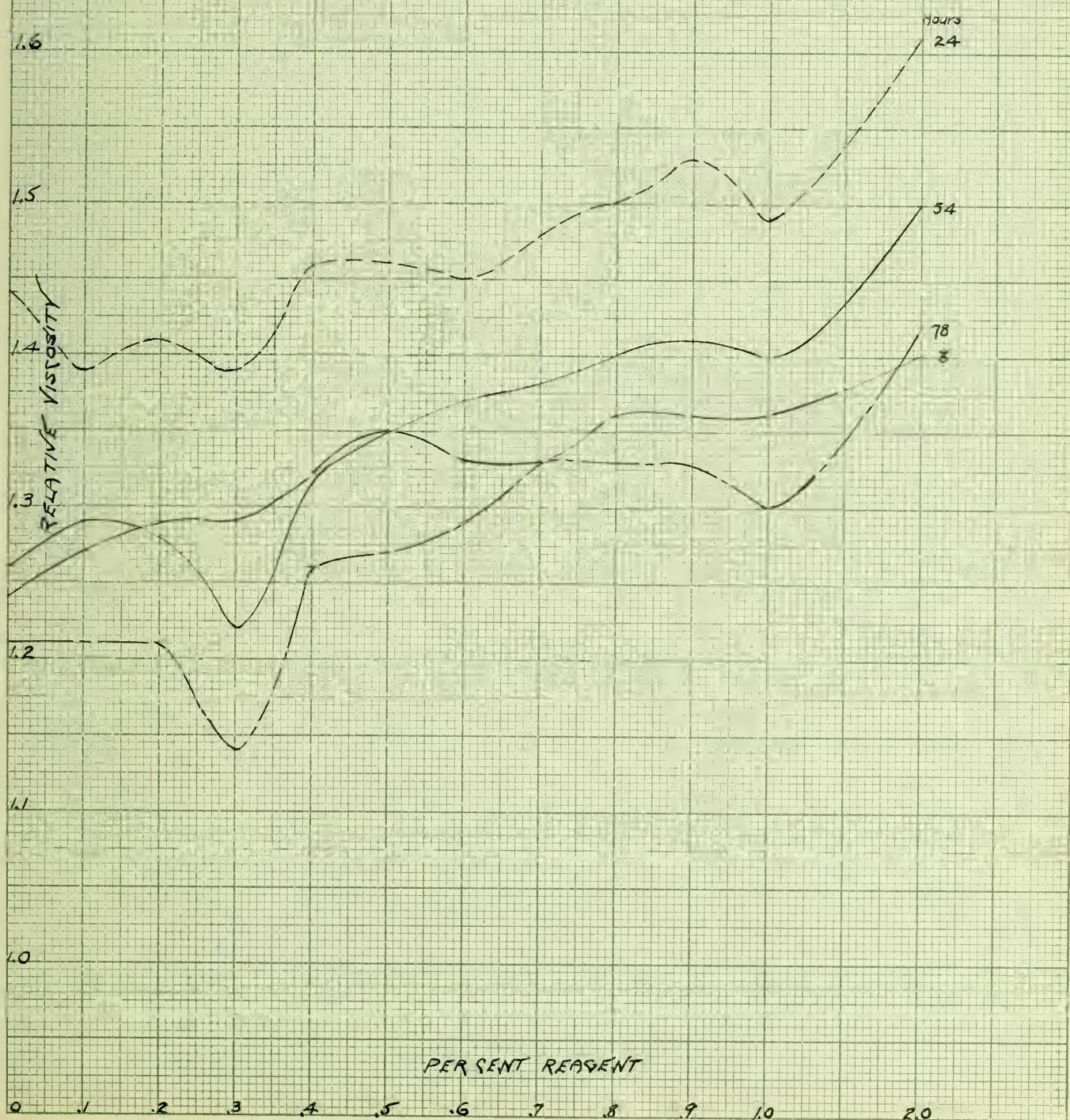
-20-

FIGURE 5
SERIES 3
$MgSO_4$
TIME-VISSOSITY
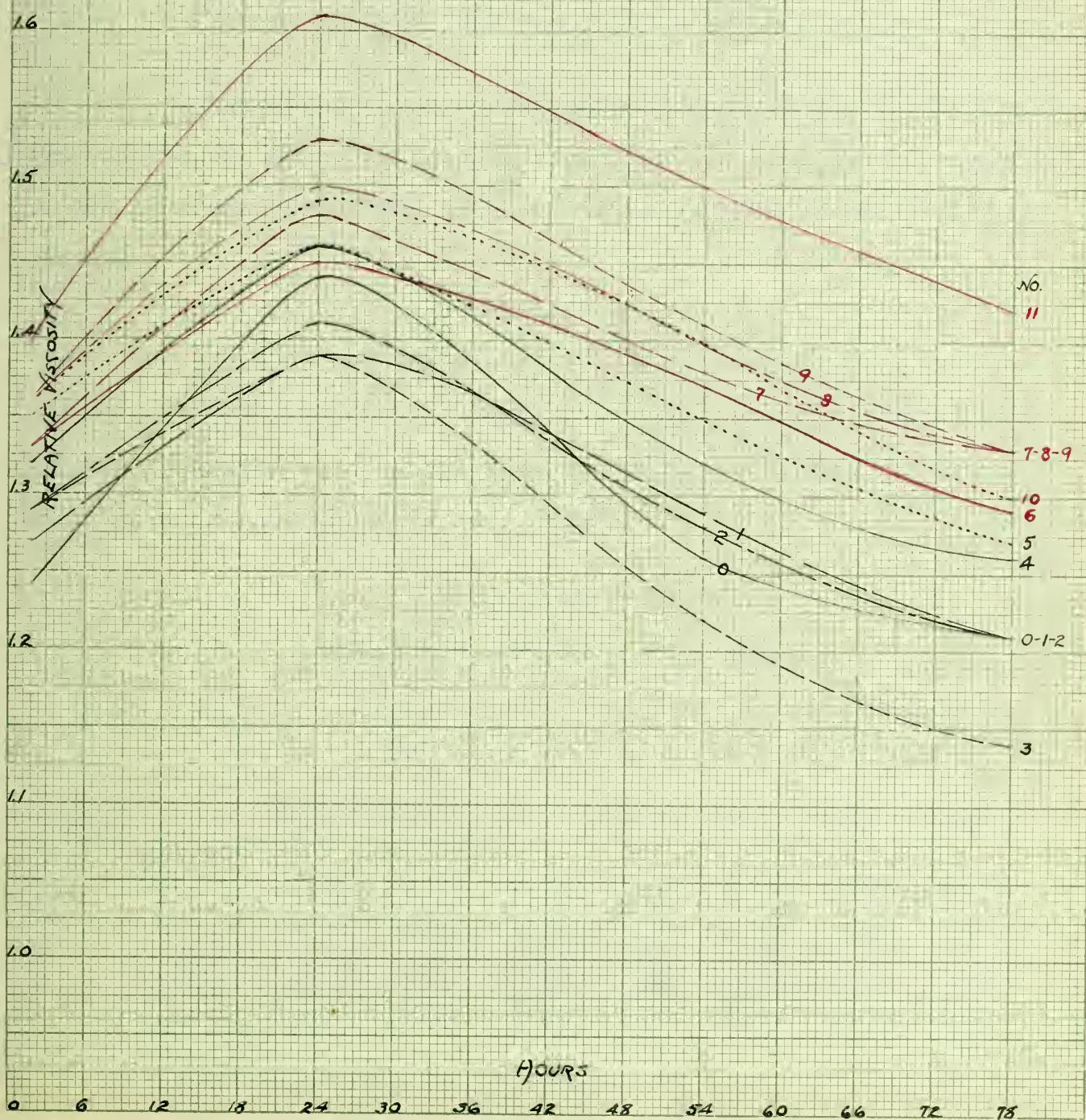
The enamels were applied in the condition in which their viscosities were measured with the result that all of the coatings were thin.

| No. | | 0 | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 | 10 | 11 |
|-----|---|---|---|---|---|---|---|---|---|---|---|----|----|
| Body | 0 | FB | G | G | G | G | G | G | G | G | G | G | G |
| " | I | F,C | G | G | G | G | G | G | G | G | G | G | G |
| " | II | F,C | F | SB | SB | F,C | F,C | F,C | F,C | F,C | F,C | F,C | F,C |

These were the most encouraging results yet obtained and the enamels on clay I especially indicated that the adhesion was due to the magnesium sulphate, because the trial with 0% had flaked and cracked.

## Series 4.

In order to obtain wider ranges in viscosities so that the effects of different per cents of reagent might be emphasized, another magnesium sulphate series was prepared in which 50 grams of solid material were used in each sample.

### VISCOSITIES - SERIES 4

$MgSO_4$ + 50 grams Solid Material.

| | | Hours | | | | | | |
|---|---|------|------|------|------|------|------|------|
| | | 1 | 17 | 41 | 64 | 90 | 112 | 165 |
| Factor | | 13.0 | 12.8 | 13.0 | 13.0 | 13.2 | 13.2 | 13.2 |
| No. | % Reagent | | | | | | | |
| 0 | 0 | 1.51 | 1.59 | 1.61 | 1.73 | 1.70 | 1.70 | 1.71 |
| 1 | .1 | 1.65 | 1.69 | 1.62 | 1.72 | 1.71 | 1.70 | 1.70 |
| 2 | .2 | 1.71 | 1.73 | 1.66 | 1.72 | 1.73 | 1.70 | 1.70 |
| 3 | .3 | 1.84 | 1.94 | 1.88 | 1.92 | 1.89 | 1.89 | 1.85 |
| 4 | .4 | 1.91 | 2.14 | 2.03 | 2.08 | 2.14 | 2.06 | 2.06 |
| 5 | .5 | 1.89 | 2.02 | 2.03 | 2.11 | 2.08 | 2.20 | 1.91 |

| 6  | .6  | 1.95 | 2.17 | 2.17 | 2.24 | 2.29 | 2.23 | 2.15 |
| 7  | .7  | 1.97 | 2.20 | 2.23 | 2.34 | 2.32 | 2.26 | 2.18 |
| 8  | .8  | 2.04 | 2.38 | 2.39 | 2.53 | 2.40 | 2.30 | 2.26 |
| 9  | .9  | 2.15 | 2.97 | 4.11 | 2.96 | 3.06 | 3.05 | 3.01 |
| 10 | 1.0 | 2.03 | 2.38 | 2.54 | 2.68 | 2.50 | 2.47 | 2.52 |
| 11 | 2.0 | 2.10 | 2.61 | 2.79 | 2.99 | 3.07 | 3.06 | 3.50 |

The lack of agreement noticeable in the corresponding curves for series 3 and 4 is evidently due principally to the differences in concentration since in series 3 forty grams of enamel were contained in 100 c.c. while fifty grams had been diluted to the same volume in series 4. The difference in time between the preparation of the enamel and its application would also exert an influence upon the fitting properties. The only similarities in Figs. 4 and 6 are the increasing viscosities and the hint in Fig. 4 of the maxima that Fig. 6 makes so distinct. Figs. 5 and 7 are equally inconsistent and exhibit no likenesses. The trials were dipped at the end of the 165 hours and gave the following results after drying:-

Body 0 - All Flaked and Cracked.

Body I - All Good.

Body II - All Flaked and Cracked.

In this series with body I, however, it was observed that the bond was better in the enamels with higher content of the sulphate. There was no adhesion between the enamels and clay I, while the bond was good in the preceeding series with exactly the same per cents of reagent but made up with more water. The final explanation for this is difficult especially since series 4 was dipped at a time when the comparative viscosities were high and series 5 when the viscosities

FIGURE 6
SERIES 4
MgSO₄
REAGENT-VISCOSITY

FIGURE 7
SERIES 4
MᵍSO₄
TIME-VISCOSITY
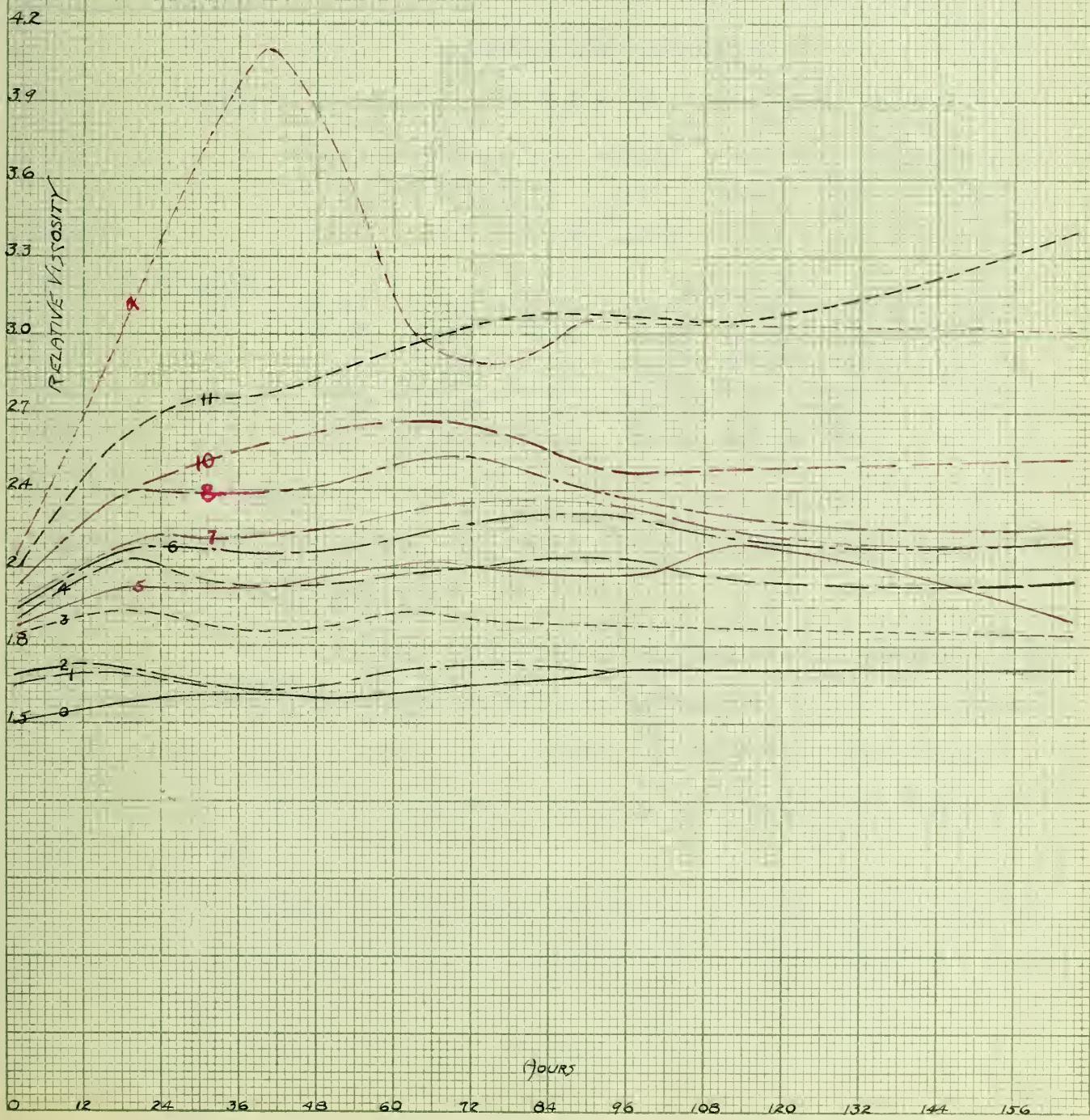
were correspondingly low.

## Series 5.

With the idea still in mind that greatest coagulation could be produced by salts containing trivalent and quadrivalent bases, another series was prepared in which potassium alum was used as the coagulant.

VISCOSITIES - SERIES 5

$K_2SO_4 \cdot Al_2(SO_4)_3 \cdot 24 H_2O$ + 50 grams Solid Material.

| | | | | | Hours | | | |
|---|---|---|---|---|---|---|---|---|
| | | 1 | 16 | 42 | 69 | 90 | 112 | 138 |
| Factor | | 12.3 | 12.2 | 12.4 | 12.0 | 14.4 | 11.5 | 12.5 |
| No. | % Reagent | | | | | | | |
| 0 | .5 | 2.60 | 3.64 | 3.96 | 4.00 | 5.00 | 5.24 | 6.48 |
| 1 | 1.0 | 3.33 | 5.00 | 5.40 | 6.75 | 10.35 | 12.53 | 65. |
| 2 | 2.0 | ----- | 6.65 | 6.93 | 10.17 | 20.83 | 36.6 | ----- |
| 3 | 3.0 | 7.80 | 24.57 | 26.80 | 45.83 | 77. | 233. | ----- |
| 4 | 4.0 | 9.02 | 19.27 | 21.77 | 32.25 | 67. | 156. | ----- |
| 5 | 5.0 | 15.11 | 27.40 | 26.65 | 7.75 | 29.88 | 156. | ----- |

At 138 hours enamels 2, 3, 4, and 5 had become too thick to flow through the Mariotte tube. No value is given for sample No. 2 at one hour because it was lost.

In Fig. 8 steady increases of viscosity are observed with increasing alum - up to 3%. With this percentage maxima are seen at all times. Fig. 9 shows that viscosity increased with time. The sudden drop and rise of the viscosity of No. 5 at 69 hours is unaccounted for.

The adhesion tests were directly contrary to expectations as all of the enamels flaked and cracked on each of the three bodies.

FIGURE 8
SERIES 5
ALUM
REAGENT VISCOSITY

-27-
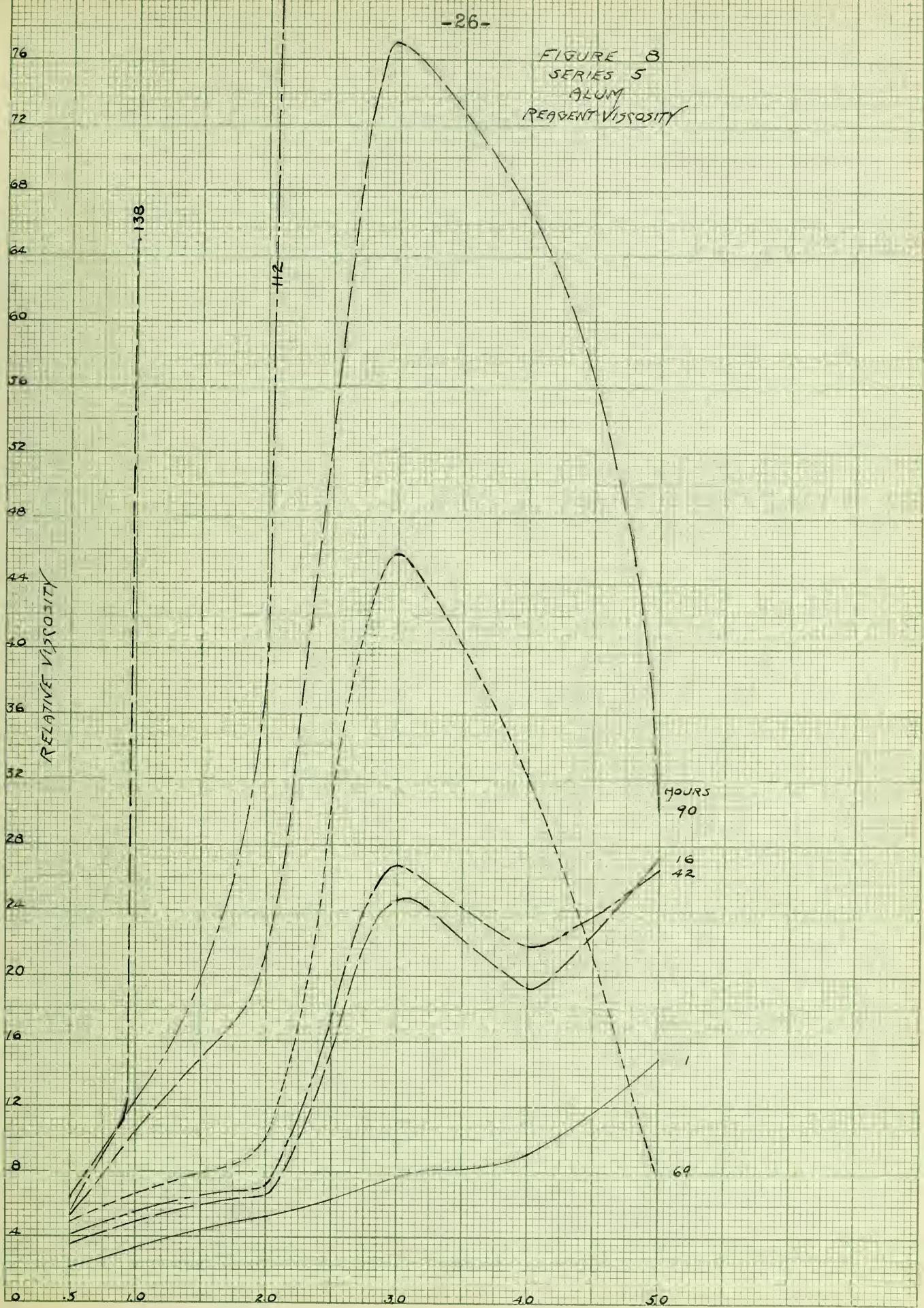
FIGURE 9
SERIES 5
ALUM
TIME - VISCOSITY

RELATIVE VISCOSITY

HOURS
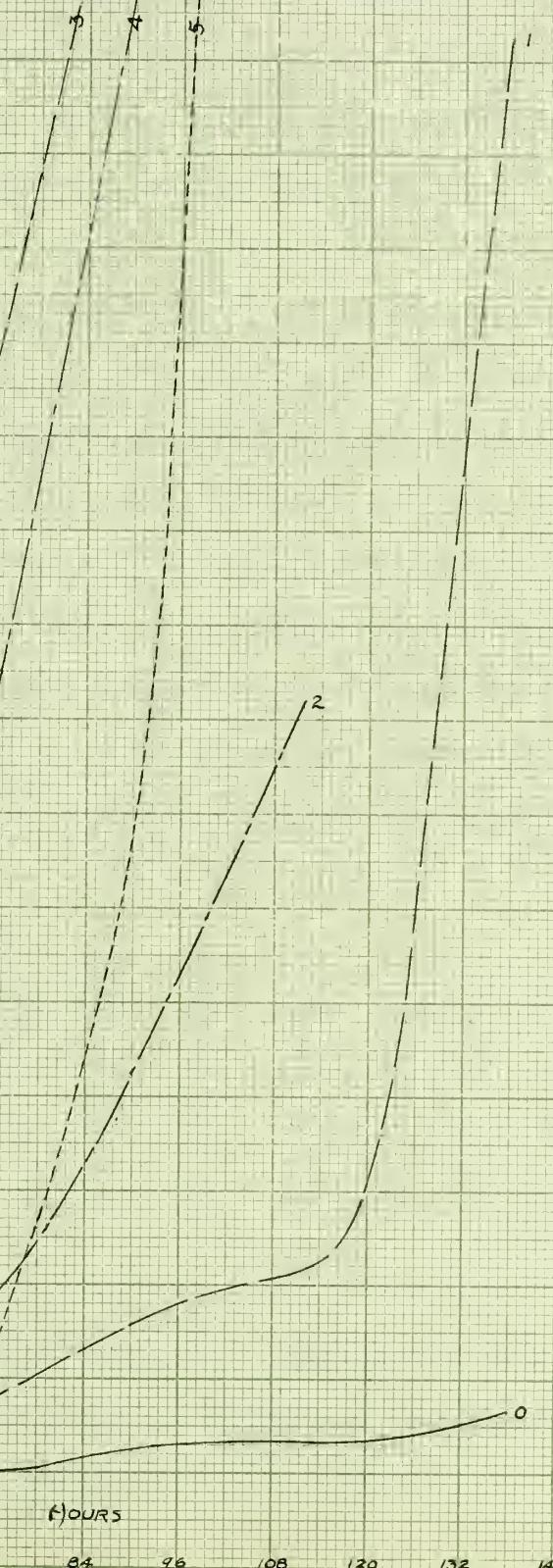
## Series 6.

No other electrolytes whose chemical properties were such that suggested favorable results could be brought to mind. Kirkpatrick and Arnold obtained their best results with silicic acid gel precipitated in the enamel by sodium silicate and oxallic acid. A series was next prepared, therefore, for the purpose of comparing results.

An analysis of the sodium silicate solution used showed .53 gram of solid matter and .405 gram of $SiO_2$ per c.c; the molecular formula, therefore, was $Na_2O \cdot 3.35 \ SiO_2$ or approximately .3 $Na_2O \cdot SiO$; and the concentration .53 gram per cc.

By dilution a solution of 100 grams per liter was obtained. A solution of oxallic acid of the same concentration was made. In order to determine what proportions of these gave the largest amount of silicic acid as a precipitate, graduated tubes were filled to the 100 c.c. mark with the combinations noted below and shaken.

| No. | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 |
|---|---|---|---|---|---|---|---|---|---|
| Oxallic acid c.c. | 10 | 20 | 30 | 40 | 50 | 60 | 70 | 80 | 90 |
| Sodium silicate c.c. | 90 | 80 | 70 | 60 | 50 | 40 | 30 | 20 | 10 |
| Precipitate c.c. | little | 100 | 100 | 100 | 3 | 1 | very little | | |
| Time of formation, Hrs. | 24 | 24 | 1/2 | 24 | 24 | 24 | 24 | 24 | 24 |

Consequently the proportions given under 3 were employed for the introduction of the silicic acid to the enamel and the per cent of reagent means the percentage by weight of the sodium silicate and oxallic acid or of the products of their interaction.

| No. | %Reagent | gms. Reagent | Oxallic Acid | Sodium Silicate |
|-----|----------|--------------|--------------|-----------------|
| 0 | .5 | .25 | .75 | 1.75 |
| 1 | 1.0 | .50 | 1.50 | 3.50 |
| 2 | 2.0 | 1.00 | 3.00 | 7.00 |
| 3 | 3.0 | 1.50 | 4.50 | 10.50 |
| 4 | 4.0 | 2.00 | 6.00 | 14.00 |
| 5 | 5.0 | 2.50 | 7.50 | 15.50 |

The enamel was weighed into cylinders, the sodium silicate added, and the whole thoroughly shaken; then the oxallic acid was introduced, and again the samples were shaken.

## VISCOSITIES - SERIES 6

Sodium Silicate and Oxallic Acid + 50 gms. Solid Material.

| | | Hours | | |
|-----|-----------|------|------|------|
| | | 2 | 23 | 47 |
| Factor | | 14.4 | 11.5 | 12.5 |
| No. | % Reagent | | | |
| 0 | .5 | 1.18 | 1.13 | 1.09 |
| 1 | 1.0 | 1.18 | 1.18 | 1.17 |
| 2 | 2.0 | 1.25 | 1.22 | 1.18 |
| 3 | 3.0 | ---- | ---- | ---- |
| 4 | 4.0 | ---- | ---- | ---- |
| 5 | 5.0 | ---- | ---- | ---- |

Trials 3, 4, and 5 were too viscous to flow through the tube.

Figure 10 shows a general though irregular increase of viscosity with increasing silicic acid; the red curves, however, show a decrease of viscosity with increasing time due, perhaps, to the general conversion of the gel to sol. Immediate dipping, therefore, would probably give better results in the adhesion tests.

-30-
FIGURE 10
SERIES 6
SODIUM SILICATE AND OXALLIC ACID.
REAGENT-VISCOSITY
TIME-VISCOSITY
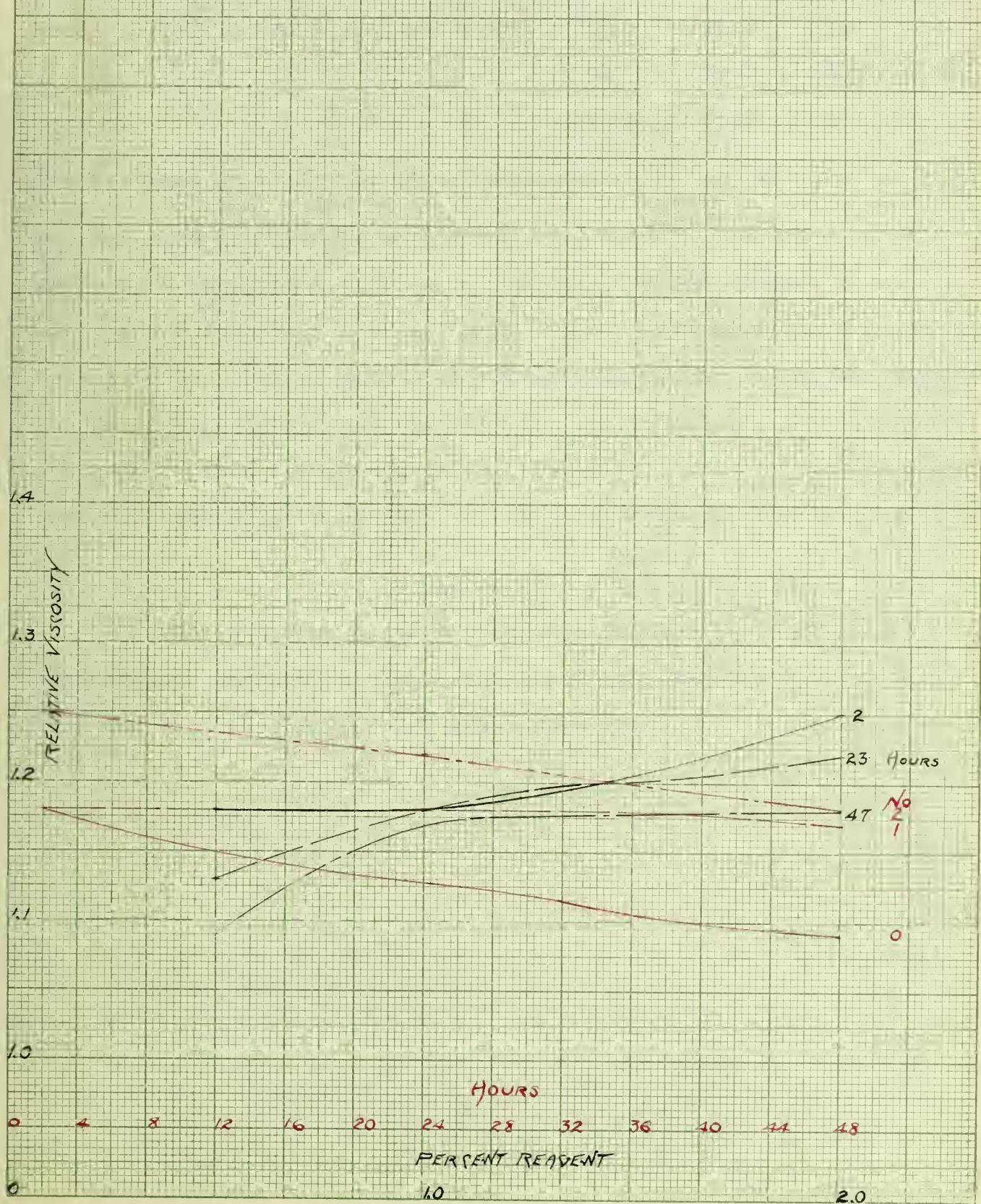
The dipped enamels dried as follows:-

| No. | | 0 | 1 | 2 | 3 | 4 | 5 |
|---|---|---|---|---|---|---|---|
| Body | 0 | Soft and incoherent | | | GB | GB,C | GB,C |
| " | I | | " | | GB | GB,C | GB,C |
| " | II | | " | | GB,C | GB,C | GB,C |

The coatings on the first three trials lay like dry flour without any cohesion between the particles. The bond in the cases of enamels 3, 4, and 5 was excellent. In each instance enamel 4 was badly cracked and 5 was slightly so. The cracking of No. 4 might be due to the greater amount of gel causing excess drying shrinkage, yet No. 5 containing more silicic acid cracked less. Kirkpatrick and Arnold found five per cent of silicic acid the minimum for good bond with the clays they used, and one of these was the same as II.

## Series 7.

While series 5 was drying another alum series was investigated. In this, however, three per cent was the maximum addition and only 40 grams of dry glaze were used.

## VISCOSITIES - SERIES 7

$K_2SO_4 \cdot Al_2(SO_4)_3 \cdot 24 \ H_2O$ + 40 grams Solid Material.

| | | Hours | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| | | 21 | 50 | 68 | 97 | 117 | 164 | 190 | 212 |
| Factor | | 11.8 | 12.0 | 12.0 | 11.8 | 14.0 | 14.0 | 14.0 | 14.0 |
| No. | %Reagent | | | | | | | | |
| 0 | .5 | 2.58 | 2.22 | 2.27 | 2.18 | 2.10 | 2.43 | 2.50 | 2.51 |
| 1 | 1.0 | 2.17 | 2.20 | 2.27 | 2.32 | 2.29 | 3.00 | 3.06 | 3.14 |
| 2 | 1.5 | 2.39 | 2.91 | 2.45 | 2.50 | 2.64 | 3.26 | 3.71 | 4.29 |
| 3 | 2.0 | 2.17 | 2.13 | 2.25 | 2.34 | 2.32 | 2.67 | 2.96 | 3.00 |
| 4 | 2.5 | 2.63 | 2.63 | 2.82 | 2.92 | 3.06 | 3.25 | 3.67 | 3.84 |
| 5 | 3.0 | 2.74 | 2.58 | 2.65 | 2.78 | 2.67 | 4.43 | 6.14 | 7.57 |

Fig. 11 shows maxima at 1.5%; as this amount was not used in series 5, Fig. 8 does not indicate them. In series 7, however, high viscosities are observed at 3%; these become maxima in Fig. 8. Figs. 9 and 12 illustrate the same time effect.

### Series 8.

Results obtained by use of silicic acid as employed in series 6 were not very successful. It was resolved then, if possible, to introduce the pure silicic acid free from sodium oxalate or other electrolytes. In the above mentioned series, sodium oxalate was a product of the interaction of the sodium silicate and the oxallic acid. This salt would act as a defloculant and tend to prevent the attainment of equilibrium by the silicic acid gel and the constituents of the enamel. To eliminate this action it was necessary to add only the pure silicic acid. This was accomplished as follows: An amount of silicic acid that would

-33-

FIGURE II
SERIES 7
ALUM
REAGENT-VISCOSITY

-34-
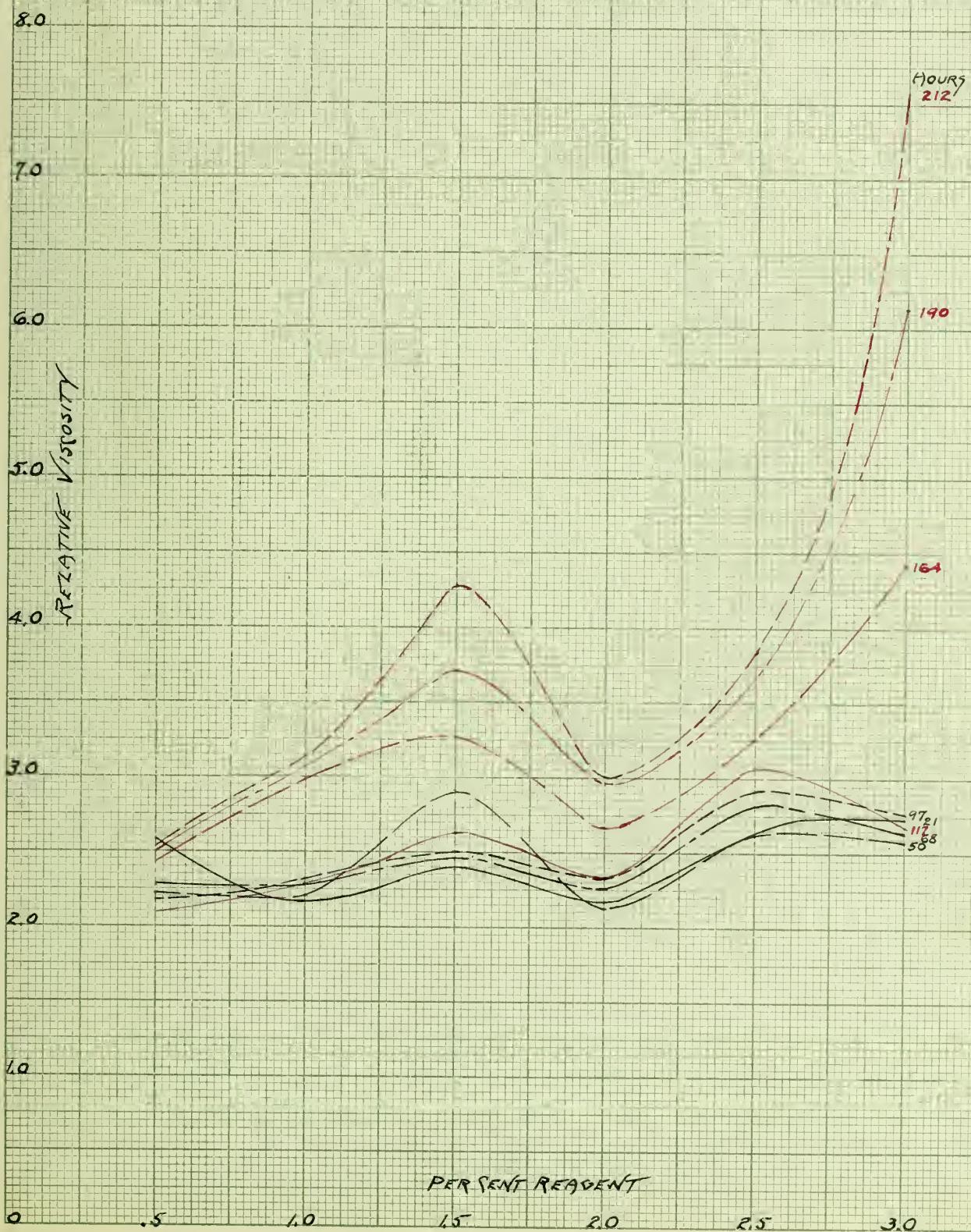
FIGURE 12
SERIES 7
ALUM
TIME - VISCOSITY
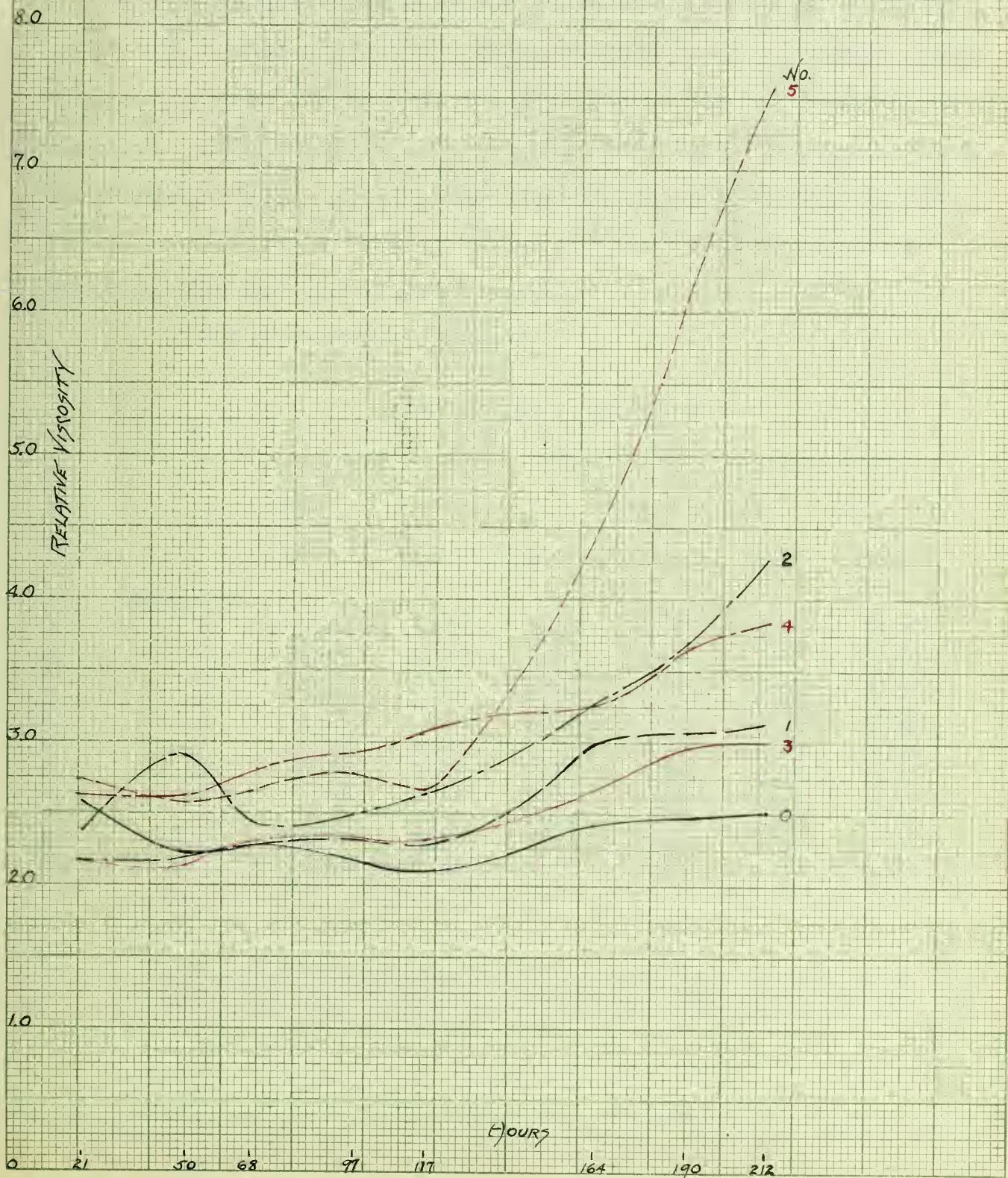
give ten grams of $H_2SiO_3$ was diluted. To this was added a slight excess of very dilute hydrochloric acid. The gel formed was washed by decantation five or six times, after which it was introduced into a ball mill with a newly weighed batch of enamel. The whole was ground for an hour and then passed through a screen of 100 mesh. After removal from the mill the enamel was particularly smooth and creamy. The moisture factor was then determined and additions of silicic acid up to one per cent were obtained by blending this and the original enamel.

The viscosities follow:

VISCOSITIES - SERIES 8

| | | Hours | | | | | |
|---|---|---|---|---|---|---|---|
| | | 45 | 71 | 93 | 143 | 191 | 213 |
| Factor | | 14.0 | 14.0 | 14.0 | 14.0 | 14.0 | 14.8 |
| No. | %Reagent | | | | | | |
| 0 | 0 | 1.89 | 1.94 | 1.89 | 2.10 | 2.41 | 2.46 |
| 1 | .1 | 1.59 | 1.57 | 1.57 | 1.59 | 1.67 | 1.63 |
| 2 | .2 | 1.61 | 1.57 | 1.53 | 1.50 | 1.50 | 1.48 |
| 3 | .3 | 1.76 | 1.70 | 1.63 | 1.57 | 1.63 | 1.51 |
| 4 | .4 | 1.87 | 1.83 | 1.74 | 1.71 | 1.73 | 1.68 |
| 5 | .5 | 2.09 | 2.01 | 1.96 | 1.90 | 1.99 | 1.92 |
| 6 | .6 | 2.33 | 2.24 | 2.20 | 2.04 | 2.53 | 2.09 |
| 7 | .7 | 2.76 | 2.66 | 2.61 | 2.37 | 2.60 | 2.49 |
| 8 | .8 | 3.40 | 3.21 | 3.19 | 3.06 | 3.10 | 3.03 |
| 9 | .9 | 3.71 | 3.59 | 3.54 | 3.41 | 3.76 | 3.58 |
| 10 | 1.0 | 4.83 | 4.74 | 4.61 | 4.31 | 4.76 | 4.45 |

| | | | | Hours | | |
|---|---|---|---|---|---|---|
| | | 237 | 261 | 289 | 310 | 385 |
| Factor | | 14.0 | 14.2 | 14.0 | 14.4 | 14.5 |
| No. | % Reagent | | | | | |
| 0 | 0 | 3.04 | 2.90 | 3.57 | 4.11 | ---- |
| 1 | .1 | 1.87 | 1.72 | 1.73 | 1.80 | 2.03 |
| 2 | .2 | 1.57 | 1.47 | 1.46 | 1.43 | 1.53 |
| 3 | .3 | 1.63 | 1.49 | 1.47 | 1.47 | 1.46 |
| 4 | .4 | 1.80 | 1.62 | 1.63 | 1.69 | 1.68 |
| 5 | .5 | 2.11 | 1.97 | 1.97 | 2.08 | 2.14 |
| 6 | .6 | 2.23 | 2.07 | 2.04 | 2.21 | 2.14 |
| 7 | .7 | 2.72 | 2.47 | 2.39 | 2.46 | 2.52 |
| 8 | .8 | 3.43 | 3.03 | 3.04 | 3.36 | 3.59 |
| 9 | .9 | 4.07 | 3.73 | 3.89 | 4.30 | 5.23 |
| 10 | 1.0 | 4.83 | 4.75 | 5.07 | 5.70 | 6.62 |

Examination of the curves of Figs. 13 and 14 shows plainly that small additions of washed silicic acid caused thinning of the slip and that amounts of at least .5% were necessary for thickening. Above this percentage, viscosity rapidly increased with small additions. Fig. 14 shows that enamels containing low per cents of silicic acid became thinner with time; while those with .8% or more thickened with age.

The results of the adhesion tests were:-

| No. | 0 | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 | 10 |
|---|---|---|---|---|---|---|---|---|---|---|---|
| Body O | F,C | F,C | F,C | F | F,C | G | F,C | G | G | G | G |
| Body I | F,C | G | G | G | G | G | G | G | G | G | G |
| Body II | F,C | F,C | F,C | F,C | F,C | F,C | F,C | F,C | F,C | F,C | F,C |

## Series 9.

The use of electrolytes had produced results that were not entirely satisfactory. Indeed those employed served as coagulators, as the viscosity tests show, yet they failed to effect any consistent or marked increase of bond between the enamels and the

FIGURE 13
SERIES 8

SILISIS ACID
REAGENT-VISCOSITY

-38-
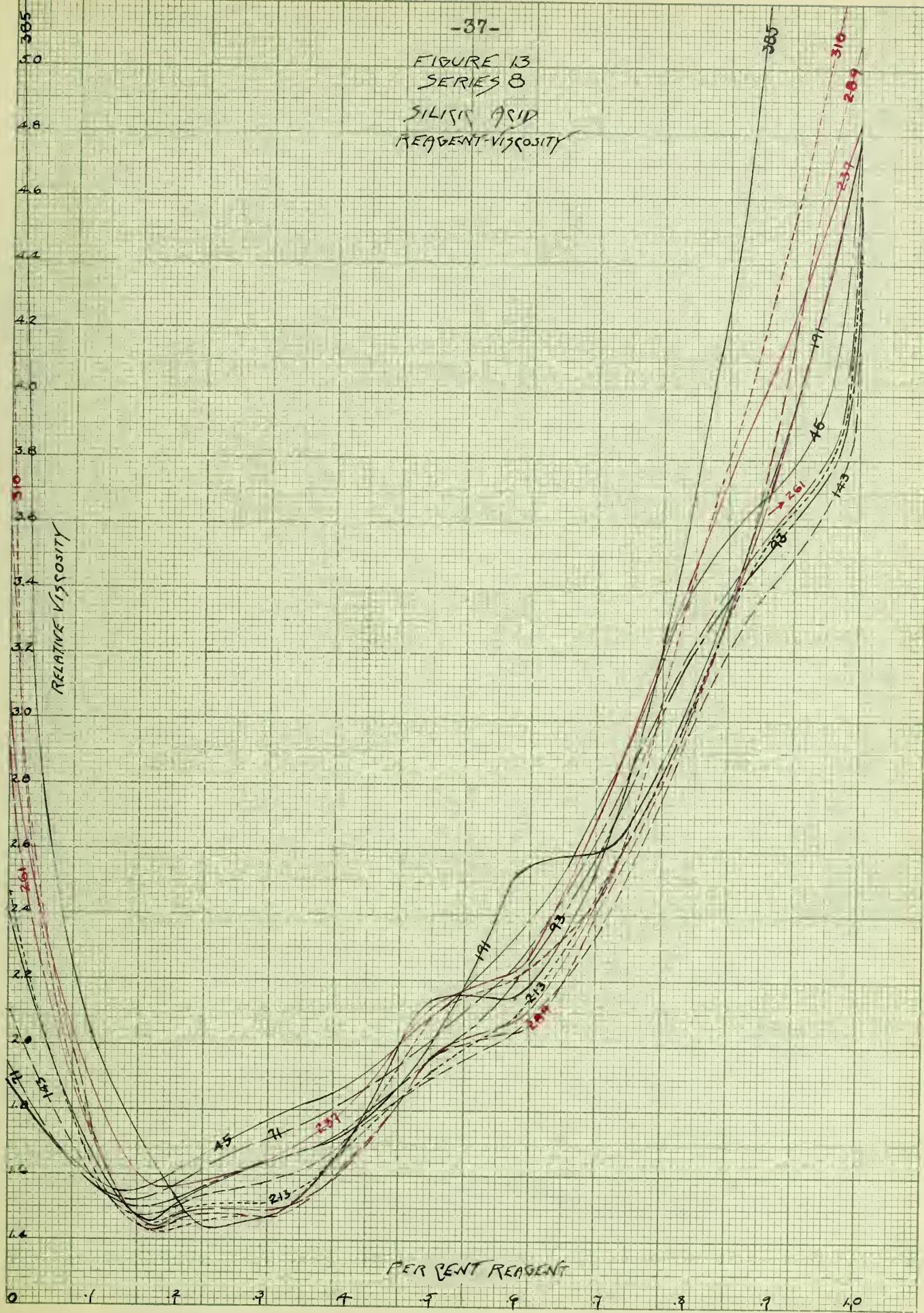
FIGURE 14
SERIES 8
SILISIS ACID.
TIME-VISCOSITY
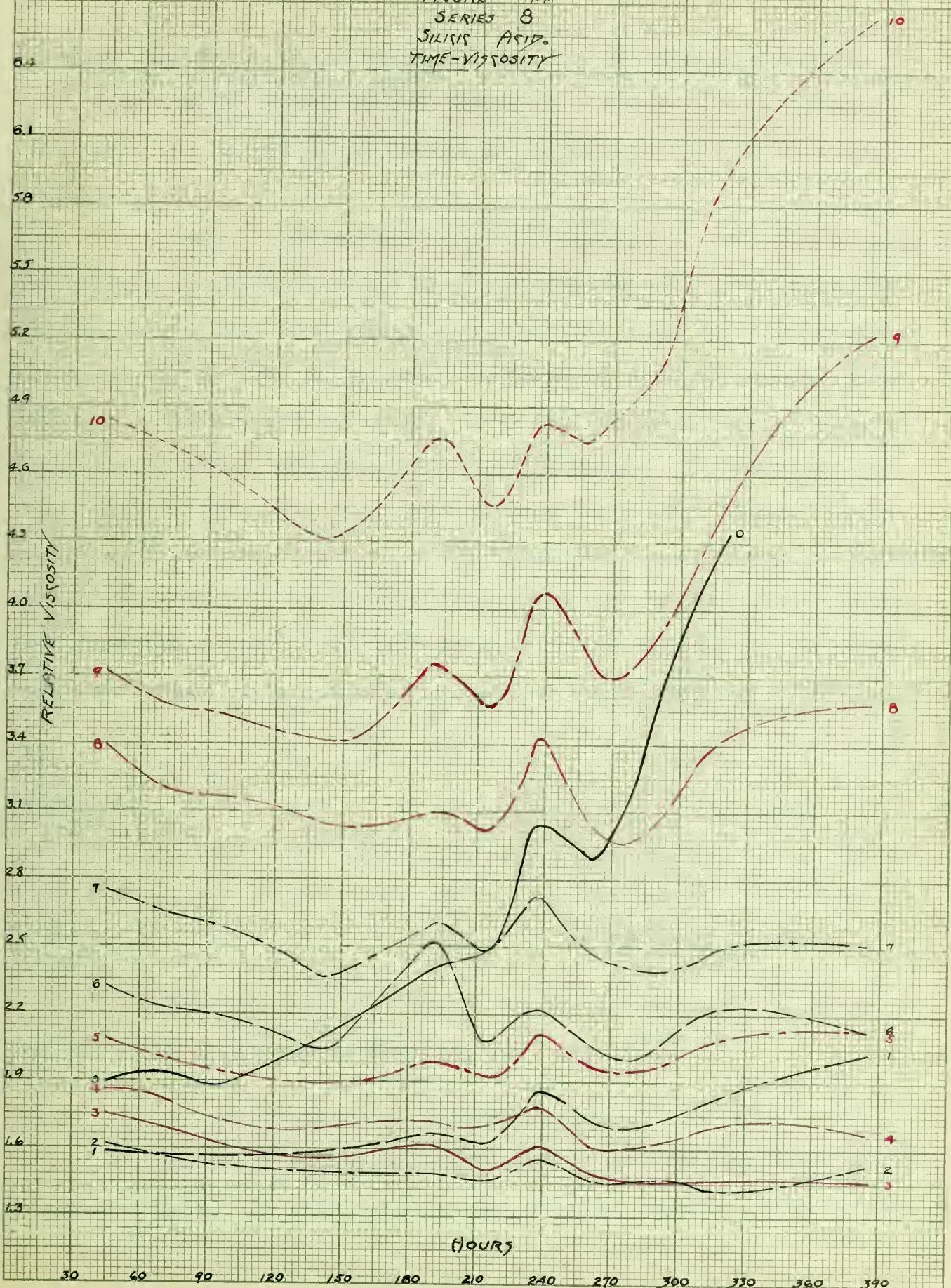
bodies. One other means remained: the use of organic colloids. The objection to these is that though they afford bond in drying, they burn out in the early stages of firing and flaking then may result.

Starch was the first one selected. Seventy grams of starch were boiled in water until a uniform pastewas obtained. This was poured into a ball mill containing a new 500 gram batch of enamel. Grinding was allowed to proceed for about an hour and a half after which the mixture was screened. A series of eight members was pre- pared by blending this and the original enamel. No viscosity de- terminations were made as it was assumed that their factors would vary in direct proportion with the amount of the colloidal gel added. After the enamel had stood for twenty-four hours most of the water was decanted; the coatings were applied rather thickly to the trials and when these had dried the following results were observed:-

| No. | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 |
|---|---|---|---|---|---|---|---|---|
| % Starch | .5 | 1.0 | 1.5 | 2.0 | 2.5 | 3.0 | 3.5 | 4.0 |
| Body 0 | SB | G | G | G | G | G | G | G |
| " I | SB | G | G | G | G | G | G | G |
| " II | NB | FB | F | F | F | GB | GB | GB |

Additions of 1% of starch to the enamel make it adhere to bodies 0 and I, but 3% is required for clay II.

### Series 10

Another starch series containing the same per cents as the above was made. In this instance the dipping was done with the en-

amels in a more fluid state to determine if the starch would give
bond when the shrinkage was greater.  The results:-

| No. | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 |
|---|---|---|---|---|---|---|---|---|
| Body O | F | G | G | G | G | G | G | G |
| " I | F | G | G | G | G | G | G | G |
| " II | F,C | G | G | G | G | G | G | G |

With clay II, therefore, better results were obtained
here than in the preceeding series.  In the former set flaking was
due to too low shrinkage of the enamel.

## Series 11.

The use of gum tragacanth was next attempted.  One gram
was soaked in water for several days; heat was then applied until
all of the lumps had softened and disappeared.  The paste was added
to a portion of the original enamel containing 100 grams of solid
material.  After thorough mixing another series was blended.  The
samples were allowed to stand for twenty-four hours, but no water
could be decanted without loss of the gum as this had risen in the
tubes above the solid matter.  Consequently the enamels were ap-
plied just as they were after thorough mixing and very thin coatings
resulted.

| No. | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 10 |
|---|---|---|---|---|---|---|---|---|---|
| % Gum | .1 | .2 | .3 | .4 | .5 | .6 | .7 | .7 | 1.0 |
| Body O | F,C | G | G | G | G | G | G | G | G |
| " I | F,C | G | G | G | G | G | G | G | G |
| " II | F,C | G | F | G | G | G | G | G | G |

Because of the thin coverings the results are not reliable as series 12 shows.

### Series 12.

The remaining portions of the samples of series 12, exclusive of No. 1, were thickened by evaporation until they would hardly pour. Trials O and II were then dipped; the results:-

| No. | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 10 |
|---|---|---|---|---|---|---|---|---|
| Body O | G | G | G | G | G | G | G | G |
| " II | F | F | F | F | F | F | F | F |

### Series 13.

While the viscosity tests were still being run on series 8, a duplicate set was prepared. The enamels were allowed to stand for twenty-four hours, after which they were made very thick by evaporation of the excess water. Heavy coatings were applied to the trials O, and these were set in the open to dry. The drying required only twenty-four hours, and in each instance the enamel was badly cracked and gave no bond. The lack of this may have been due to the extreme rate of drying, the thickness of the coating, or perhaps to the heating of the enamel.

### Series 14.

Fig. 5 illustrated so well that magnesium sulphate produces maximum viscosity of the enamel in twenty-four hours that it was decided to make another series containing this reagent to be applied after the enamels had stood for one day. Dipping of the

trials of clay O occurred twenty-six hours after the reagent had been added.  In order to thicken the samples sufficiently, water was decanted although it was found that this would remove some $MgSO_4$ , but, however, after it had served its purpose.  Drying progressed fairly rapidly.  The table gives the results:-

| No. | O | 1 | 2 | 3 | 4 | 5 |
|---|---|---|---|---|---|---|
| % Reagent | .2 | .4 | .6 | .8 | 1.0 | 2.0 |
| Body  O | F,C | F,C | SB | F,C | F,C | F,C |
| "   I | FB | F,C | FB | SB | F,C | FB |
| "   II | F,C | FB | F,C | F,C | F,C | F,C |

## Series  15.

The remaining portions of the samples of series 14 were applied to trials that were subjected to a comparatively severe drying test; i.e., exposure in the open.  The results:-

| No. | O | 1 | 2 | 3 | 4 | 5 |
|---|---|---|---|---|---|---|
| Body  O | F,C | F,C | F,C | F,C | F,C | F,C |

The results of Series 14 and 16 demonstrate that $MgSO_4$ is of practically no value, despite the conclusions drawn from series 3 and 4.

## Series  16.

After another twenty-four hours trials were dipped with the remaining samples (series 8) and these too were dried quickly.

| No. | O | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 | 10 |
|---|---|---|---|---|---|---|---|---|---|---|---|
| Body O | F,C | G | G | G | G | G | G | G | G | G | G |

All of the dried trials that exhibited sufficient bond between body and glaze to stand ordinary handling were burned in an oil-fired test-kiln. The pieces were set on edge so that if flaking occurred in burning it could easily be observed. The time of burning was twenty hours and the heat attained was such that cone 7 was down and cone 8 half over. The trials fired were:-

| Series | Body | Trial numbers. |
|--------|------|----------------|
| 1  | O   | O |
| 1  | I   | 0,1,2,3,7,8, |
| 3  | O   | 0,1,2,3,4,5,6,7,8,9,10,11 |
| 3  | I   | 1,2,3,4,5,6,7,8,9,10,11 |
| 3  | II  | 2,3 |
| 4  | I   | 0,1,2,3,4,5,6,7,8,9,10,11 |
| 6  | O   | 3,4,5, |
| 6  | I   | 3,4,5 |
| 6  | II  | 3,4,5 |
| 9  | O   | 2,3,4,5,6,7,8 |
| 9  | I   | 2,3,4,5,6,7,8 |
| 9  | II  | 2,6,7,8 |
| 10 | O   | 1,2,3,4,5,6,7,8 |
| 10 | I   | 1,2,3,4,5,6,7,8 |
| 10 | II  | 2,3,4,5,6,7,8 |
| 11 | O   | 2,3,4,5,6,7,8,10 |
| 11 | I   | 2,3,4,5,6,7,8,10 |
| 11 | II  | 2,3,4,5,6,7,8,10 |
| 12 | O   | 2,3,4,5,6,7,8,9,10 |
| 16 | O   | 1,2,3,4,5,6,7,8,9,10 |

The results of the burn are indicated briefly in the following:-

Series 1 - Cracked, bubbled, and poorly covered.

Series 3 - Somewhat bubbled; very thin.

Series 4 - Badly bubbled and blistered.

Series 6 - Badly beaded - body cracked.

Series 9 - With the exception of No. 7 of Body II all held well. The enamel was not very smooth; somewhat higher firing, however, would have softened the glaze sufficiently to remedy this. The

coating was of such thickness and opacity as to completely hide the body.

Series 10 - The coatings were thinner in this series, yet the enamel ran on body II. On 0 and I, however, the results were similar to those of the previous series.

Series 11 - Held well but too thin.

Series 12 - Enamels 3, 4, 5, and 7 held perfectly; 2 and 6 ran slightly and 8 and 10 badly.

Series 16 - All ran badly.

The trials of series 8 were not dry enough to be burned with the others. Series 16, containing the same reagent, demonstrated that defective adhesion would have resulted. From series 9 and 10 it is noted that for bodies 0 and I starch gives the requisite bond during drying and the enamel shows no evidence of flaking in burning. Additions of about 1% are necessary, as the enamel with only .5% flaked during the drying. Series 11 and 12 indicate that as low as .3 or .4% of gum tragacanth will suffice for making the enamel adhere to body 0; too high a percentage is to be avoided if we may judge from trials 8 and 10. Body II, however, which has proven extremely difficult to fit, was not dried successfully in series 12 but dried well in 11 where the coatings were extremely thin. The burned trials of this body were not satisfactory.

IV

## SUMMARY.

The results of this investigation intimate that it is possible to fit an enamel to a plastic clay body not through the use of the electrolytes stannic chloride, magnesium sulphate, or alum but by the addition of the organic colloids starch or gum tragacanth.

All of the electrolytes employed herein have caused coagulation of the colloids in our enamel suspension but have not produced sufficient adhesion between enamel and body.

In general, increasing amounts of these electrolytes increased the viscosity although maxima often appeared at intermediate points on the curves. With small amounts of reagent, as a rule, little variation in viscosity was observed in the daily tests; with higher percentages, however, the usual effect of time was to increase the viscosity.

The precipitation of silicic acid gel in the enamel, as Kirkpatrick and Arnold found, might result in success in some instances. The defect of beading that occurred in the burning probably could be overcome without destruction of the bond. Washed silicic acid proved a failure in producing bond that would withstand the fire.

The best results were obtained with starch and gum tragacanth, especially the former. For most bodies, in all probability, amounts of one per cent of the former and somewhat smaller amount of the latter would prove adequate.